THE ULTRAVIOLET ABSORPTION SPECTRA OF PHENETOLE AND *n*-BUTYLBENZOATE IN DIFFERENT STATES *

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ABSTRACT. The absorption spectra of phenetole in the liquid and solid states and those of *n*-butylbenzoate in the vapour, liquid and solid phases have been photographed in the region between 2820 and 2500 A U., using thin films of the substances in the case of the liquid and solid phases

In the absorption spectrum of phenetole in the liquid state at 30 C, three broad bands are observed with the ν_0-band at 35771 cm^{-1} and other bands corresponding to a progression of vibrational frequency 901 cm^{-1} In the solid state at −180 C the broad bands observed for the liquid state become much sharper and each is accompanied by three faint bands. The bands correspond to the vibrational frequencies 500, 773, 932, 945 and 1272 cm^{-1} and their combinations The ν_0-band in the solid state at −180°C is shifted towards longer wavelengths by 38 cm^{-1} from its position in the liquid state and by 629 cm^{-1} from its position in the vapour state

The absorption spectrum of *n* butylbenzoate in the vapour state yields 9 bands with the ν_0-band at 36009 cm^{-1} and progression of vibrational frequencies 360 and 944 cm^{-1} and their combinations In the liquid state at 32°C the substance yields only three bands corresponding to vibrational frequency 952 cm^{-1} and the whole spectrum is shifted by about 573 cm^{-1} towards longer wavelengths. When the liquid is solidified and cooled to −180°C the bands shift by about 100 cm^{-1} towards longer wavelengths and become a little sharper.

These results have been discussed in detail.

INTRODUCTION

The investigations of the absorption spectra of some aromatic organic compounds in different states and at different temperatures carried out recently in this laboratory (Deb, 1951, 1952, 1953 : Sirkar and Swamy 1952 ; Swamy 1952, 1953) yielded results which furnish much information regarding the influence of the intermolecular field on the electronic energy levels of the molecules in the liquid and solid states. The investigations referred to above were mainly confined to substituted benzene compounds and a few double-ring compounds. Yet the changes taking place in the absorption spectra with change of state were found to be of widely different characters for different molecules with, of course, some characteristics common to all the substances. For example, the ν_0-band and the spectrum as a whole are

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shifted towards longer wavelengths in all the cases with the change from vapour to liquid state. The number of bands also become much smaller with liquefaction of the vapour, but the subsequent changes taking place in the spectrum on solidification of the substances are found to be different for different molecules. In some cases the electronic energy level is split up into several components with solidification and lowering of temperature of the substances (Sirkar and Swamy 1952, Swamy 1952). In the case of other molecules such as diphenylmethane, dibenzyl (Deb 1953), *p*-dichlorobenzene (Swamy, 1952), etc., the bands due to the liquid phase become sharper in the spectrum due to the solid state at low temperature, and as a result of this sharpening some weak bands due to $0-v$ transitions, which are absent in the case of the liquid phase, are distinctly resolved in the spectra due to the solid phase. The sharpening of the bands were attributed to cessation of angular oscillations of the molecules in the crystal at low temperatures.

There is still a third group of compounds, the absorption spectra of which do not undergo the changes mentioned above with the change of state from liquid to solid phase. Methyl and ethyl benzoates were found to belong to this group (Deb, 1951*b*, 1953).

Further, the shift of the ν_0-band with solidification in the case of all compounds studied so far was found to be different from each other in magnitude and direction, for different compounds. The vibrational frequencies for the excited state were also found to be changed in the case of some compounds with solidification and lowering of temperature of the substances.

The investigations were continued in order to get information regarding other compounds and the present paper reports the results obtained in the case of phenetole ($C_6H_5OC_2H_5$) and *n*-butylbenzoate ($C_6H_5COOC_4H_9$). The data obtained in the case of phenetole have been compared with those in the vapour state reported by Sreeramamurty (1951) and in the other case the spectra for all the three states have been investigated.

EXPERIMENTAL

The experimental technique used in these investigations has been described previously (Deb, 1951*a*). The ultraviolet continuum was obtained from a hydrogen discharge tube run at about 3 K. V. The thickness of the absorbing film in the solid and liquid states, required for the production of bands in the absorption spectrum was about a few microns in the case of phenetole and less than 0.1 mm in the other case. For investigations at low temperatures a Dewar vessel made of fused silica was used as before.

The substances studied were of chemically pure quality. Phenetole was supplied by B. D. H. and *n*-butylbenzoate by Fisher Scientific Co. of U. S. A. They were redistilled in evacuated double bulbs before use.

The length of the of the absorption tube used in the investigation of the spectrum of *n*-butylbenzoate in the vapour state was 90 cm, the ends being closed by quartz windows, sealed with sodium silicate cement. A Cenco

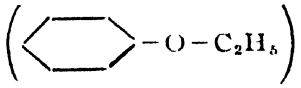
Hyvac pump was used to evacuate the tube. The temperature of the tube as well as the bulb containing the liquid, connected to the tube was maintained much above room temperature by playing the flame of a burner over the tube and bulb intermittently.

All the photographs were taken on Ilford H. P. 3 films using a Hilger E 1 quartz spectrogrph which has a dispersion of about 3 A.U. per mm in the region, 2600 Å. Iron arc comparison was recorded in each photograph and microphotometric records of the spectra were taken using a Kipp and Zonen self-recording microphotometer. In each record a known iron line at one end of the spectrum was taken as the reference line. The wavelengths of the bands were calculated from these records from the known ratio used (1.6 : 1) and the distance of peaks from the reference line mentioned above.

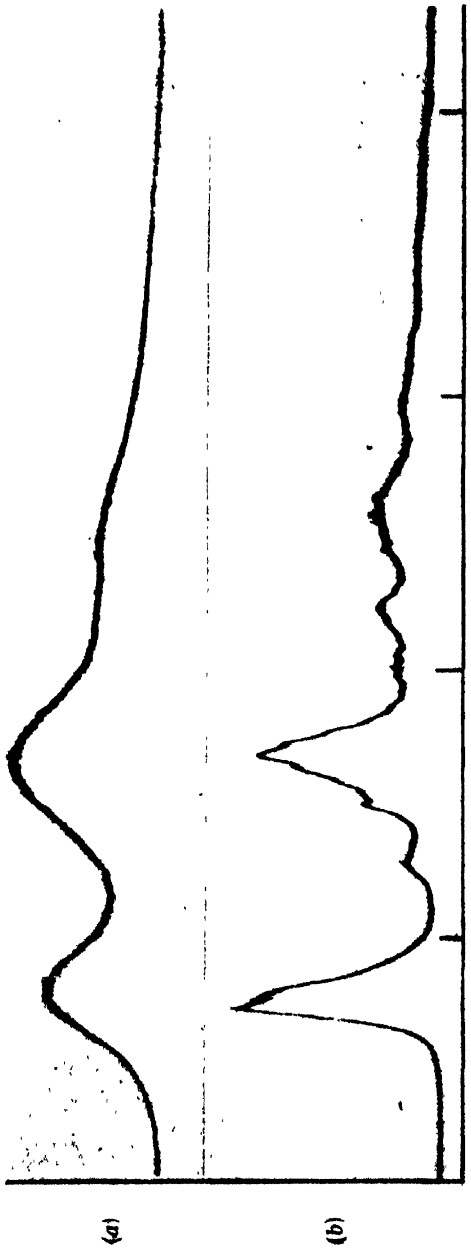
RESULTS AND DISCUSSION

The microphotometric records of the spectra have been reproduced in figures 1 and 2 and the wave numbers of the bands and their assignments are given in Tables I and II. For comparison, the wave numbers and assignments of several prominent bands of phenetole in the vapour state, reported by Sreeramamurty (1951) have been included in columns 1 and 2 of Table I. Column 3 of the same table gives the exicited state frequencies of phenetole vapour reported by Robertson, *et al* (1950).

TABLE I

Ultraviolet absorption bands of phenetole ()

Vapour (Sreeramamurty, (1951 (Prominent bands only)		Vapour (Robertson *et al*, 1950)	Liquid at 30°C (Present author)		Solid at −180°C (Present author)	
ν (cm^{-1}) and Int.	Assignment	Excited st frequencies (cm^{-1})	ν (cm^{-1}) and Int.	Assignment	ν (cm^{-1}) and Int	Assignment
36362 (vvs)	ν_0	155 (w)	35771 (vs)	ν_0	35733 (vvs)	ν_0
36916 (ms)	ν_0+554	340 (w)			36203 (ms)	ν_0+560
37106 (vs)	ν_0+744	760 (vs)			36506 (s)	ν_0+773
37130 (ms)	$\nu_0+744+27$	940 (vs)	36672 (vvs)	ν_0+901	36635 (w)	ν_0+902
		1255 (m)			36678 (vvs)	ν_0+945
37269 (vs)	ν_0+907				37005 (w)	ν_0+1272
37314 (ms)	ν_0+952	The ν_0 band			37239 (ms)	$\nu_0+945+560$
37625 (vs)	ν_0+1272	at 36352 cm^{-1}	37572 (w)		37449 (w)	$\nu_0+945+773$
				$\nu_0+2\times901$	57625 (ms)	$\nu_0+2\times945$
					37953 (w)	$\nu_0+945+1272$
					38182 (vw)	$\nu_0+2\times945+560$
					38561 (vvw)	$\nu_0+3\times945$
					38898 (vvw)	$\nu_0+2\times945+1272$



Microphotometric records of the ultraviolet absorption spectra of phenetole

FIG. 1

(a) Liquid at 30°C (b) Solid at −180°C

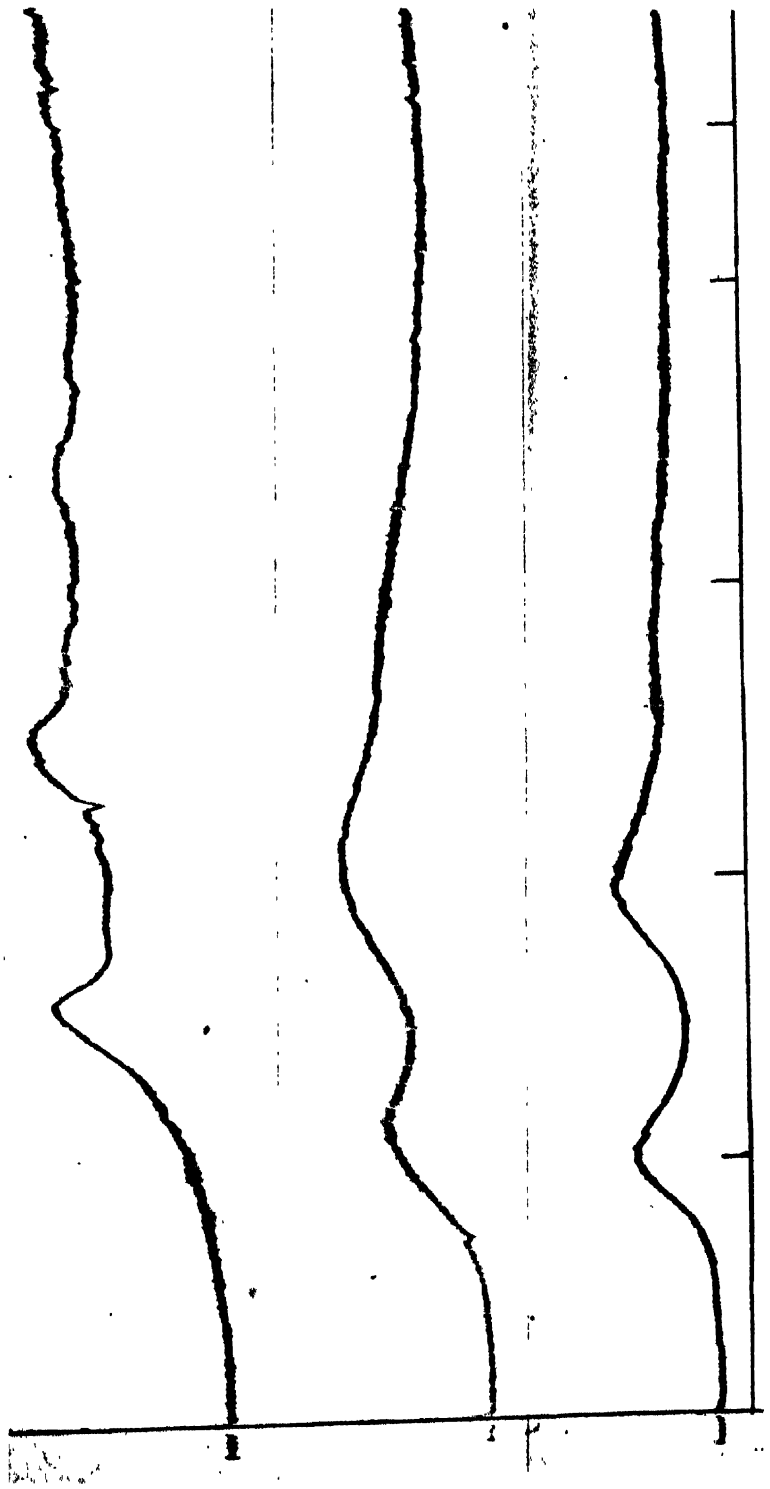
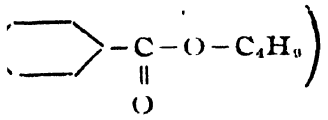


FIG. 2

(a) Vapour (b) Liquid at 30°C (c) Solid at −180°C

TABLE II

Ultraviolet absorption bands of *n*-butylbenzoate 

Vapour		Liquid at 32°C		Solid at -180°C	
ν (cm^{-1}) and Int.	Assignment	ν (cm^{-1}) and Int.	Assignment	ν (cm^{-1}) and Int.	Assignment
35703 (vvw)	ν_0-396				
36099 (vs)	ν_0	35627 (vs)	ν_0	35526 (vs)	ν_0
36459 (w)	ν_0+360				
37043 (vvs)	ν_0+944	36579 (vvs)	ν_0+952	36478 (vs)	ν_0+952
37400 (w)	$\nu_0+944+360$				
37986 (s)	$\nu_0+2\times944$	37526 (w)	$\nu_0+2\times952$	37428 (w)	$\nu_0+2\times952$
38348 (vw)	$\nu_0+2\times944\times360$				
38920 (vw)	$\nu_0+3\times944$				
39290 (vvw)	$\nu_0+3\times944+360$				

Phenetole:

It is seen from Table I as well as from figure 1 that the fine structure of the bands of phenetole vapour reported by Sreeramamurty (1951) is completely absent in the spectrum of the substance in the liquid state, Only three broad bands are present in the liquid state. The first one on the longer wavelength side, which is at 35771 cm^{-1} is taken as the ν_0-band. The ν_0-band in the vapour state (Sreeramamurty, 1951) is at 36362 cm^{-1}. Thus there is a shift of the ν_0-band by about 391 cm^{-1} towards longer wavelengths with the liquefaction. The only vibrational frequency in the excited state observed in the case of the liquid state is 901 cm^{-1} measured from these broad bands. In the case of the solid phase at −180°C, the broad bands of the liquid phase become much sharper, so that several other feeble bands which are merged in the broad bands in the spectrum of the liquid state are clearly resolved out. The vibrational frequency 901 cm^{-1} deduced from the centres of the broad bands in the case of the liquid state is found to be resolved into two bands at 902 and 945 cm^{-1} in the case of the solid state. The other new bands are found to have frequency-differences 560, 773 and 1272 cm^{-1} from the ν_0-band and their combinations with the frequency 945 cm^{-1} or its harmonics. These bands, therefore, are due $o-v$ transitions and not due to the splitting of electronic energy levels. Some of the excited state frequencies observed in the case of the vapour (Sreeramamurty, 1951) are 554, 744, 907, 952 and 1252 cm^{-1}. Robertson, *et al* (1950) reported the excited state frequencies 760, 940 and 1255 cm^{-1} besides a few more, in the case of the vapour state. But there is one significant difference between the spectrum due to the vapour and that due to the solid. It is quite evident that the bands representing the frequencies 560, 773 and 1272 cm^{-1} in the case of the solid state are much weaker than the corres-

ponding bands observed in the case of the vapour. Thus the transitions are restricted by neighbouring molecules in the solid state. The sharpening of the bands observed in this case is evidently due to cessation of some motions of the molecules in the lattice, which, as has been pointed out earlier (Swamy, 1952 ; Deb, 1953) might be the angular oscillations of the molecules. The influence of the intermolecular field on the electronic energy level is clearly indicated by the shift of the ν_0-band with liquefaction. The cessation of angular motions of the molecules is probably caused by the formation of virtual bonds between neighbouring molecules. The shift of the ν_0-band is towards longer wavelengths both with liquefaction of the vapour and solidification of the liquid phase in this case, and this may indicate a gradual strengthening of the virtual bands with lowering of temperature.

The absorption spectrum of anisole, the lower homologue of phenetole is exactly similar to that of phentole in the liquid state. In the solid state, however, they are not exactly similar. In the case of anisole only one more vibrational frequency, in addition to that of the liquid state was observed in the solid state at low temperature (Deb, 1951*a*) ; whereas in the present case three more vibrational frequencies and several combination frequencies are also observed.

n-Butylbenzoate :

In the vopour state *n*-butylbenzoate yields 9 bands. The strong and sharp band on the long wavelength side of the spectrum at 36099 cm^{-1} has been assigned as the ν_0-band of the system. The othre bands are then found to correspond to vibrational frequencies 360 and 944 cm^{-1} and their harmonics and combinations. One very feeble band on the long wavelength side of the ν_0-band is observed at a distance of 390 cm^{-1} from the ν_0 band. This band is totally absent in the spectra due to the liquid and solid states. Evidently, this represents a ground state vibrational frequency which probably fall to the value 360 cm^{-1} in the excited state.

In the liquid state at 32°C, the substance yields only three broad bands, the distance between the centres of the successive bands being 952 cm^{-1}. The ν_0-band shifts towards longer wavelengths by 472 cm^{-1} from its position in the vapour state, when the vapour is liquefied. When the substance is solidified and cooled to −180°C, the bands again shift towards longer wavelengths, the shift of the ν_0-band being 100 cm^{-1}. No further changes are observed in this case, except a slight sharpening of the bands with lowering of temperature to −180°C. The vibrational frequency 944 cm^{-1} in the vapour state remains practically the same in the liquid and solid states in this case.

These results are similar to those observed in the case of ethylbenzoate (Deb, 1953) and methylbenzoate (Deb, 1951*b*). The influence of the intermolecular field thus lowers the excited state energy levels of these molecules,

this lowering for the change from vapour to liquid phase being much larger than that for the change from liquid to solid phase. The absence of any appreciable sharpening of bands at −180°C points out that the angular motions of the molecules, which are supposed to be the cause of the broadening of bands in the liquid state, persist in this case even at −180°C. The linking of the molecules wih the neighbouring ones at low temperatures is thus less favoured in this case than in the case of phenetole. From an observation of similar results in the case of ethylbenzoate it was suggested that the shape of the molecule might be the determining factor in allowing the formation of virtual bonds in such a way that angular motions of the molecules are very much restricted. Evidently, in all these benzoic acid esters the presence of the flexible groups C-O-C_2H_5 etc. is responsible for the fluctuation of intermolecular field even in the solid state at −180°C. The ν_0-band is a little sharper in these cases than the other bands. This shows that the vibrational transitions of the molecules broaden the electronic energy level in the excited state.

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